

Europäisches Patentamt

Eur pean Patent Office

Office ur péen des brevets



EP 0 748 876 A1

(12)

# **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

18.12.1996 Bulletin 1996/51

(51) Int. Cl.6: C22C 14/00, B23K 35/32

(21) Application number: 96108929.9

(22) Date of filing: 04.06.1996

(84) Designated Contracting States: DE GB NL

(30) Priority: 16.06.1995 JP 150753/95 16.06.1995 JP 150758/95 16.06.1995 JP 150779/95

(71) Applicant: DAIDO TOKUSHUKO KABUSHIKI KAISHA Naka-ku Nagoya-city Aichi-prefecture (JP) (72) Inventors:

 Shimizu, Takao Tenpaku-ku, Nagoya-city, Aichi-pref. (JP)

 Asari, Seiya Machida-city, Tokyo (JP)

 Yokota, Norlyoshl Nakamura-ku, Nagoya-city, Aichi-pref. (JP)

(74) Representative: Reinhard - Skuhra - Weise & Partner
Postfach 44 01 51
80750 München (DE)

(54) Titanium alloy, member made of the titanium alloy and method for producing the titanium alloy member

(57) A titanium alloy of which crystal grain is hard to coarsen at the time of welding or hot-extruding, which consists by weight percentage of at least one element selected from  $0.01 \sim 10$  % of S,  $0.01 \sim 10$  % of Se and  $0.01 \sim 10$  % of Te (the total sum does not exceed 10 %), one or both of  $0.01 \sim 10$  % REM and  $0.01 \sim 10$  % of Ca (the total sum does not exceed 10 %), and if necessary, at least one element selected from Al  $\leq 10$  %, V  $\leq 25$ %, Sn  $\leq 15$ %, Co  $\leq 10$ %, Cu  $\leq 10$ %, Ta  $\leq 15$ %, Mn  $\leq 10$ %, Hf  $\leq 10$ %, W  $\leq 10$ %, Si  $\leq 0.5$ %, Nb  $\leq 20$ %, Zr  $\leq 10$ %, Mo  $\leq 15$ %, and  $0 \leq 0.1$ % (the total sum does not exceed 30 %).

EP 0 748 876 A1

#### Descripti n

## **BACKGROUND OF THE INVENTION**

#### Field of the Invention

This invention relates to a titanium alloy excellent in weldability or joinability as a material for various titanium alloy members such as a pipe or so used in industrial fields of aerospace, chemistry, oil well drilling and the like, and further relates to a method for producing the titanium alloy members such as the titanium alloy pipe and a joined tubular body made of the titanium alloy.

## Description of the Prior Art

Generally, a titanium alloy is superior in strength per unit mass and excellent in corrosion resistance and the like, therefore it has been used widely in industrial fields of aerospace, chemistry, oil well drilling and so on.

The titanium alloy or titanium alloy member is joined through various joining methods such as TIG welding (tungusten inert gas arc welding), MIG welding (metal inert gas arc welding), friction welding, electron beam welding, laser beam welding, diffusion welding, brazing and the like.

In any joining methods, however, the titanium alloy base metal adjacent to the joined zone changes its property and; noit deteriorates in its mechanical properties owing to the thermal effect at the time of joining, and it is difficult to ensure joint strength equivalent to the strength of the base metal in most cases. Accordingly, there has been a problem in that development of a titanium alloy of which quality is not deteriorated so remarkably by the thermal effect at the time of the joining is earnestly cried for.

On the other hand, in order to further make the most use of the excellent characteristics of the titanium alloy in the aforementioned industrial fields, it is dispensable to manufacture titanium alloy pipes from the titanium alloy. However, as conventional techniques for manufacturing the titanium alloy pipes, a few methods have been merely put to practical use, such as a method of bending the titanium alloy formed in a thin sheet into an O-like shape through a U-like shape and joining a seam of the titanium alloy sheet bent in the O-like shape, and a method of forming the titanium alloy pipe directly by cutting a titanium alloy block through machining.

However, in a case of the welded pipe which is manufactured by joining the seam of the titanium alloy sheet subjected to the so-called U-O bending, there is a problem in that it is difficult to manufacture the pipe with a thick wall since there is a limit in forming of the titanium alloy sheet.

Further, there is another problem in a case of the titanium alloy pipe by machine cutting in that cost of the pipe increases because the yield rate of the titanium alloy material and the production efficiency are remarkably low, though there is large room for selecting shapes and sizes.

Furthermore, it is also indispensable to join the titanium alloy pipes with each other in order to use the titanium alloy pipes as structural members. In the case of joining the titanium alloy pipes with large diameters and thick walls through the TIG welding or so, it takes considerably much time for the welding. Besides, it becomes difficult to ensure the quality of the welded joint especially in the joining at the job site, accordingly there is another problem in that it is restricted to apply the titanium alloy pipes to large-sized structures required for the joining at the job site indispensably.

### SUMMARY OF THE INVENTION

This invention has been made in view of the aforementioned problems of the prior art, it is an object to provide a titanium alloy excellent in the joinability of which quality is not deteriorated so remarkably owing to the thermal effect in the joining.

It is another object of the invention to provide a titanium alloy pipe which is excellent in surface quality and flattening test property, does not waste dies so much and is possible to be especially applied to the large-sized structures, and a method for producing such the titanium alloy pipe.

Furthermore, the other object of this invention is to provide a joined tubular body and a method for producing such the joined tubular body which are possible to improve the quality of the welded joint even in the joining at the job site and possible to be applied especially to the large-sized structures.

That is, the titanium alloy according to this invention is characterized by consisting essentially by weight percentage of not more than 10 % in total sum of at least one element selected from 0.01 to 10 % of S, 0.01 to 10 % of Se and 0.01 to 10 % of Te, not more than 10 % in total sum of one or both of 0.01 to 10 % of REM and 0.01 to 10 % of Ca, and the remainder being substantially Ti. The titanium alloy according to this invention may be further contained with not more than 30 % in total sum of at least one element selected from not more than 10 % of Al, not more than 25 % of V, not more than 15 % of Sn, not more than 10 % of Co, not more than 10 % of Cu, not more than 15 % of Ta, not more than 10 % of Mn, not more than 10 % of Hf, not more than 10 % of W, not more than 0.5 % of Si, not more than 20 % of Nb,

30

35

45

not more than 10 % of Zr, not more than 15 % of Mo and not more than 0.1 % of O according to demand.

The titanium alloy pipe according to another aspect of this invention is characterized by having a composition comprising essentially by weight percentage of not more than 10 % in total sum of at least one element selected from 0.01 to 10 % of S, 0.01 to 10 % of Se and 0.01 to 10 % of Te, not more than 10 % in total sum of one or both of 0.01 to 10 % of REM and 0.01 to 10 % of Ca, and the remainder being substantially Ti. The titanium alloy pipe according to this invention may be added with not more than 30 % in total sum of at least one element selected from not more than 10 % of Al, not more than 25 % of V, not more than 15 % of Sn, not more than 10 % of Co, not more than 10 % of Cu, not more than 15 % of Ta, not more than 10 % of Mn, not more than 10 % of Ht, not more than 10 % of W, not more than 0.1 % of Si, not more than 20 % of Nb, not more than 10 % of Zr, not more than 15 % of Mo and not more than 0.1 % of O when necessary.

In an embodiment of the titanium alloy pipe according to this invention, the pipe may be seamless. Further, in another embodiment of the titanium alloy pipe according to this invention, it is desirable according to circumstances that the ratio (t/D) of thickness (t) to outer diameter (D) of the pipe is not less than 0.01 and not more than 0.40.

The method for producing a titanium alloy pipe according to the outer aspect of this invention is characterized by extruding a titanium alloy material having the composition according to claim 1 or 2 into a seamless tubular shape.

In an embodiment of the method for producing a titanium alloy pipe according to this invention, it is desirable according to circumstances that the ratio (t/D) of thickness (t) to outer diameter (D) of the pipe is not less than 0.01 and not more than 0.40. In the other embodiments of the method for producing a titanium alloy pipe according to this invention, it is desirable to extrude the titanium alloy material at a temperature not lower than 900 °C and not higher than 1150 °C, preferably using a vitreous lubricant when occasion demands.

The joined tubular body according to the other aspect of this invention is characterized by joining the titanium alloy pipes according to claim 3 or claim 4 with each other, or by joining the titanium alloy pipe according to claim 3 and the titanium alloy according to claim 4 with each other.

In an embodiment of the joined tubular body according to this invention, the pipes may be seamless. In another embodiment of the joined tubular body according to this invention, the ratio (t/D) of thickness (t) to outer diameter (D) of the pipes may be not less than 0.01 and not more than 0.40.

The method for producing a joined tubular body according to the other aspect of this invention is characterized by comprising the steps of forming a joint layer of which melting point  $(M_i)$  is lower than melting point  $(M_M)$  of titanium alloy pipes to be joined with each other on one or both of joint faces of the titanium alloy pipes and/or inserting a joint metal of which melting point  $(M_i)$  is lower than melting point  $(M_M)$  of the titanium alloy pipes to be joined with each other between the joint faces of the titanium alloy pipes, and joining the titanium alloy pipes with each other by heating the pipes at a temperature (T) higher than  $(M_i)$  and lower than  $(M_M)$  and holding the pipes at the temperature (T) for a predetermined period at the same time of applying pressure on the joint faces of the titanium alloy pipes to be joined with each other, or by comprising the steps of inserting a joint member between joint faces of titanium alloy pipes to be joined with each other, the joint member being previously formed with joint layers of which melting point  $(M_i)$  is lower than melting point  $(M_M)$  of the titanium alloy pipes on both ends faces thereof, and joining the titanium alloy pipes with each other by heating the pipes at a temperature (T) higher than  $(M_i)$  and lower than  $(M_M)$  and holding the pipes at the temperature (T) for a predetermined period at the same time of applying pressure on the joint faces of the titanium alloy pipes to be joined with each other.

In embodiments of the method for producing a joined tubular body according to this invention, the joint metal and the joint layer may be formed in a thickness of not less than 1 µm and not more than 100 µm, and may consist essentially of Ti, Zr, Cu and Ni with the proviso that Ti and Zr are not less than 20 wt% respectively, the total sum of Ti and Zr is not less than 40 wt% and not more than 90 wt%, and the total sum of Cu and Ni is not less than 10 wt% and not more than 60 wt%.

In the other embodiments of the method for producing a joined tubular body according to this invention, the titanium alloy pipes can be heated at the temperature (T) through high-frequency induction heating in a frequency not higher than 200 kHz preferably in a vacuum or inert gas in which oxygen content and nitrogen content are not higher than 0.01 % in volume, respectively.

Further in the other embodiments of the method for producing a joined tubular body according to this invention, the pipes may be joined in a state where the joint faces of the pipes are inclined and may be joined by using a joining apparatus provided with a heating means for heating the joint faces of the titanium alloy pipes, a temperature measuring means for measuring a temperature at the joint faces of the pipes, a pressing means for applying pressure on the joint faces of the pipes, a pressure measuring means for measuring the pressure applied on the joint faces of the pipes and a control means for controlling the respective means.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIGS.1A to 1E are schematic illustrations showing arrangement of the joint metal, joint layer and joint member for joining the titanium alloy pipes in examples of this invention;

FIGS.2A to 2D are schematic illustrations showing arrangement of the joint metal, joint layer and joint member for joining the titanium alloy pipes by inclining joint faces of the pipes in the other examples of this invention; and arepsilonFIG.3 is a schematic illustration showing an example of the joining apparatus to be used in examples of this inven-. . . .

---

## **DETAILED DESCRIPTION OF THE INVENTION**

In the titanium alloy and the titanium alloy pipe according to this invention, which have the chemical composition as described above, sulfides and inclusions in the titanium alloy containing S finely disperse in granular forms by adding REM (rare earth metals) into the titanium or titanium alloy and nuclei of grain growth disperse widely in the titanium alloy. Whereby coarsening of crystal grain at a high-temperature region higher than  $\alpha$ - $\beta$  transition temperature is suppressed and coarsening of crystal grain in the base metal of the titanium alloy caused by thermal effect in joining is inhibited. Accordingly, mechanical property at the joined zone of the titanium alloy is prevented from the deterioration caused by the thermal effect at the time of joining the titanium alloy.

Even in cases of applying high upset pressure on the base metal such as a case of the friction welding, plastic deformability in the vicinity of joined zone is maintained by the inhibition of the coarsening of crystal grain, therefore defects such as cracks in the joined zone become hard to generate and the performance of the welded joint is improved.

Furthermore, generally in a case of producing the titanium alloy pipe by hot-extruding the titanium alloy material, though deformation resistance decreases and the manufacturing becomes easy by extruding the material at a temper admin ature region of β-phase, the toughness and ductility of the titanium alloy is degraded by the coarsening of crystal grain. However, the addition of REM into the titanium alloy is very effective to inhibit the coarsening of crystal grain at the temperature region higher than  $\alpha$ - $\beta$  transition temperature as mentioned above, accordingly, the titanium alloy material containing REM and S is extruded easily without degradation of the toughness and ductility.

Additionally, the sulfides and inclusions dispersed finely and uniformly work effectively for preventing exidation of the titanium alloy at the time of hot-extruding, and are rich in affinity with vitreous materials used for lubrication and effective to suppress separation of the lubricant during hot-extruding. Accordingly, surface of the titanium alloy pipe becomes fine and the extruding die is reduced in its abrasion and damage.

The aforementioned effects of REM and S are similarly confirmed also in Ca as well as REM and in Se, Te as well as S.

The reason why the chemical composition (weight percentage) of the titanium alloy or titanium alloy pipe according to this invention is limited will be described below together with functions of the respective elements.

#### S. Se and Te

5

15

20

30

40

50

Each of S, Se and Te forms inclusions in the titanium alloy by being contained not less than 0.01 % respectively, 35 and acts as nuclei of grain growth at the time of  $\alpha$ - $\beta$  transformation, thereby preventing the crystal grains from the coarsening. However, they deteriorate deformability of the alloy at a high-temperature region remarkably and degrades the extruding workability when they are contained excessively. Therefore, the upper limits of these elements are defined as 10 % respectively, and the upper limit of the total sum of these elements is also defined as 10 % in a case of combinational addition.

#### REM and Ca

In this invention, REM means Sc, Y and lanthanoid series (Atomic No.57 ~ 71). These rare earth metals combine with S, Se and Te to form stable compounds, and have a function to inhibit the coarsening of crystal grain in heat affected zone at the time of joining or the coarsening of crystal grain at the time of extruding the titanium alloy material into a tubular shape by dispersing the compounds as granular inclusions. Such the function of REM is obtained by containing not less than 10 % of any one or more of REM, however the upper limit of REM is defined as 10 % since strength and corrosion resistance of the titanium alloy or the titanium alloy pipe are deteriorated by containing them excessively.

Ca also combines with S. Se and Te to form stable compounds and has a function to inhibit the coarsening of crystal grain similarly to REM, accordingly the lower limit of Ca is defined as 0.01 %. However if Ca is contained excessively, the strength and the corrosion resistance are deteriorated similarly to the case of REM, therefore the upper limit of Ca and the upper limit of the total sum of Ca and REM are defined as 10 %, respectively.

## Al, V, Sn, Co, Cu, Ta, Mn, Hf, W, Si, Nb, Zr, Mo and O

All of these elements are useful for improving the strength of the titanium alloy or the titanium alloy pipe. Al, Sn, Co, Cu, Ta, Mn, Hf, W, Si and Nb among these elements improve the strength of the titanium alloy or the titanium alloy pipe by forming compounds with Ti, however excessive addition of above-mentioned elements damage the plastic deform-

ability of titanium alloy or the titanium alloy pipe and degrade the extruding workability and toughness. Therefore, 10 % of Al, 15 % of Sn, 10 % of Co, 10 % of Cu, 15 % of Ta, 10 % of Mn, 10 % of Hf, 10 % of W, 0.5 % of Si, and 20 % of Nb are defined as upper limits of the respective elements.

Zr, Mo and V are added in the titanium alloy in order to control the crystal grain of the titanium alloy and to obtain reasonable strength and the plastic deformability, but  $\beta$ -phase is stabilized owing to excessive addition of the elements. Accordingly, 10 % of Zr, 15 % of Mo and 25 % of V are defined as upper limits of the respective elements.

Furthermore, although O improves the strength of the titanium alloy or the titanium alloy pipe, the alloy or the pipe is embrittled by excessive addition of O, therefore the upper limit of O is defined as 0.1 %.

The plastic deformability of the titanium alloy is damaged and the toughness is deteriorated if the total sum of Al, V, Sn, Co, Cu, Ta, Mn, Hf, W, Si, Nb, Zr, Mo and O is too much, therefore the total sum of these elements is limited to not more than 30 %.

Ratio (t/D) of thickness (t) to outer diameter (D) of pipe

المدارية والأرازية ومعاصري

The lower limit of the ratio (t/D) is defined as 0.01 because the less ratio (t/D) of thickness (t) to outer diameter (D) of pipe, the more equipment cost mounts up owing to increase of required extruding force and scaling up of the equipment. The upper limit of the ratio (t/D) is defined as 0.40 because the titanium alloy pipe with a large ratio (t/D) can be manufactured also by machining and the titanium alloy pipe having an excessively large ratio (t/D) is not so valuable industrially.

# Extruding temperature

٤,

15

20

30

35

40

45

50

In a case where the titanium alloy material is extruded at a low temperature, friction between material and die becomes larger owing to large deformation resistance of the material even in a case of using lubricants, so that damage of the die and deterioration of surface quality of products are caused. Therefore, the lower limit of the extruding temperature is defined as 900 °C. Contrary to this, in a case where the extruding temperature is high, it becomes impossible to avoid a mischievous influence caused by the coarsening of crystal grain nevertheless the coarsening of crystal grain is suppressed by adding the respective elements, and the upper limit of the extruding temperature is defined as 1150 °C.

## **EXAMPLES**

## Examples 1 ~ 40

Round rods (20 mm in diameter) of the titanium alloys having compositions shown in Table 4 to Table 10 were joined through TIG welding under the condition shown in Table 1, friction welding under the condition shown in Table 3, respectively. Subsequently, obtained welded joints were subjected to tensile test and bending test, and evaluated by comparing with the specific value of the respective titanium alloy base metals. Obtained results are also shown in Tables 4 to 10 collectively.

Table 1

Welding condition of TIG welding								
Filler metal	The same composition as respective titanium alloy base metal (1.6 mm in diameter)							
Welding current	150 A							
Shielding gas	Ar							
Flow rate of shielding gas	30ℓ/min							

Table 2

Condition of friction welding

Rotational frequency of main shaft 3000 r.p.m

Frictional pressure 150 MPa

Friction time 10 sec

Upset pressure 200 Mpa

Upset time 5 sec

· -- Table 3

Condition of diffusion welding						
Joining temperature	800 °C					
Holding time	7.2 ksec					
Welding pressure	3 МРа					
Degree of vacuum 1 x 10 <sup>-6</sup> Torr						

## Table 4

No.		1	2	3	. 4	5	6
Distinction		Comparative	Comparative	Inventive	Inventive	Inventive	Inventive
Distinction		Example	Example	Example	Example	Example	Example
	s	0.005	0.10	0.01	0.1	1	5
,	REM	10	_	0.01	2	. 5	10
	Se		- :	· _	<b>-</b> .		
Chemical	Te	_	_		_	_	
Composition	Ca	_	_		_		
(wt%)	Al		_		_	6	6
(1100)	V		_		_	4	4
	Sn	_				_	
	Co		<del>;</del>		_	_	
	Cu	_	_	_	_	<u>-</u> ·	. —
	Ta			<u> </u>	_	_	_
	Mn	_ :	-	_	_	_	
	Hf	_	_	_	_	_	
	W	<del> </del>				_	
	Si		_	_	_	_	
	Nb	<del>   </del>	_	_	_	ı	
	Zr	<del>                                     </del>	_	_	-		
ļ	Mo	_	_	-			
	0	_	_	<del></del>		<del></del>	
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Joining Met	hod	TIG Welding	TIG Welding	TIG Welding	TIG Welding	TIG Welding	TIG Weldin
Joint Stren	gth	1.0	1.0	1.0	1.0	1.0	1.0
Location of	1	Fused line	Fused line	No Fracture	No Fracture	No Fracture	No Fractur
Bending Test	Piec	A	· Δ·		_0	0	0

Table 5

Inventive Example 10 10	Comparative Example 15 15	Comparative Example 0.005 0.006 0.005	Inventive Example 0.10	Inventive Example 0.01	Inventive Example 0.01
10 10    6	15 15 —	0.005 0.006	0.10	0.01	Example
10    6	15 —	0.006			0.01
6			2		
6		0.005		0.01	0.01
6			0.005	0.01	0.01
	1	_	0.005	·	0.01
	-	_	0.005		
4	6	_	_		
. 😘 -	. 4.		_	<u> </u>	
<del>-</del>	,		<u>.</u>		· -
	_	_	<del>-</del> :		
_	_	. —	<b>-</b> .:	_	
	_	_	_	_	_
	_	_		_	.,
_				_	
	_	-	-	_	
_	<u> </u>	_	_	· <b>—</b>	
	-	_	_	_	
_	_	_	<b>-</b>	_	
	_	_	<del>-</del>	_	–
	_	_	_	_	_
Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
TIG Welding	Friction Welding	TIG Welding	TIG Welding	TIG Welding	TIG Welding
1.0	0.8	1.0	1.0	1.0	1.0
No Fracture	Joint Face	Fused line	No Fracture	No Fracture	No Fracture
l l					0
No	Fracture				in tracting

# Table 6

No.	7 7	13	14 %	15	16	17	18
Distinction	Septential	Inventive	Inventive	Inventive	Inventive	Comparative	Comparative
	wet the	Example	Example	Example	Example	Example	Example
	s	0.1	2	5	3	10	5
	<del></del>	2	5.	7	10	10	
	REM	0.01	0.1	2	3	5	2
	Se			3	4	_	5
Chemical	Te	0.01	3	3		_	10
Composition		0.01		6	6	6	6
(wt%)	A1			4	4	4	4
	V	<u> </u>					
	Sn			<del> </del>	····	i	
	Co						_
	Cu		<del></del>				
	Ta					_	
	Min					<del> </del>	
	Hf						
1	W						<del> </del>
· ·	Si	-				<del> </del>	+
	Nb					<del>                                     </del>	<del> </del>
	Zr					<del>                                     </del>	+
	Mo					<del> </del>	<del></del>
	0					<del> </del>	Bal.
	e Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Friction
Joining Me	thod	TIG Welding	TIG Welding	1 '	Friction	Friction	1.
				Welding	Welding	Welding	Welding
Joint Stre	ngth	1.0	1.0	1.0	1.0	0.9	0.8
Ratio							<del></del>
Location o	f						
Fracture i		No Fracture	No Fracture	No Fracture	No Fracture	Joint Face	Joint Face
Bending Tes		el			<u> </u>		
Evaluation					0_	×	×

**Table 7**5. 200/40

No.		19	20	21	22	23	24
Distinction		Comparative	Comparative	Inventive	Inventive	Inventive	Inventive
		Example	Example	Example	Example	Example	Example
	s	0.005	0.005	0.01	0.1	1	2
	REM	0.005	0.005	0.01	1	2	5
	Se	_	0.005	0.01	_	2	4
Chemical	Te	_	0.005	_	1	_	1
Composition	Ca	_	0.005	_	2	4	3
(wt%)	Al	6	6	4	10	6	8
	V	6	6.	22	20	_	1
	Sn	2	<b>' 2</b> -	<del>-</del>		2	
	Co		_	<del>-</del>	-:	<u> </u>	:
	Cu	_	_	_	<u> </u>		
	Ta	_	_		_	_	
	Mn		_	_	_	_	. 6
•	Hf		_	_	_	<del></del> .	3
	Я	. —	_	_	- '	_ :	7
	S.i	· <b>—</b>	<del>-</del> .	_	_		0.2
	Мb	_	_	· <del>_</del>	_		4
	Zr	<del></del>	_	_	-	4	5
	Mo		<del>-</del>	-	_	2	1
	0			_	_	_	-
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Joining Meth	od	TIG Welding	TIG Welding	TIG Welding	TIG Welding	TIG Welding	TIG Welding
					٠.		,,,,,
Joint Streng	th	1.0	1.0	1.0	1.0	1.0	1.0
Ratio					,		
Location of						·	. ,
Fracture in		Fused line	Fused line	No Fracture	No Fracture	No Fracture	No Fracture
ending Test	Piece				,		٠.
Evaluation		Δ	Δ	0	0	0	0

10 '

# Table 8

		25	26	27	28	29	30
lo			Inventive	Inventive	Inventive	Inventive	Inventive
istinction"		Example	Example	Example	Example	Example	Example
	<del></del> -	3	7	2	1	2	2
= •	S		10	7	10	3	7
	REM	<del></del>		5	8	1	
•	Se			3	0.01	1	5
hemical	Te	7		2		_	_
Composition	-			7	4		
(wt%)	Al				25	_	
	V	<u></u>		1		15	
	Sn	l :		2			10
	.00	<u></u>		4			10
	Cri	7				15	
	Ta	10		2			10
	Mn			1			_
	Hf	1		5			<del></del>
1	W		<u> </u>				
	Si	\		1	_		
	<del></del>			1			
	Zr			-			
	Mo	10	<u> </u>		1	<del>-</del> .	
	. 0	0.5	<u> </u>		Bal.	Bal.	Bal.
· <u> </u>	T1		Bal.	Bal.	Friction	Friction	Friction
Joining Me	thod	Friction	Diffusion	Diffusion		Welding	Welding
	<u>.</u>	Welding	Welding	Welding	Welding 1.0	1.0	1.0
Joint Stre	ngth	1.0	1.0	1.0	1.0	1.0	
Ratio					ļ		
Location of		No Fracture	No Fracture	No Fracture	No Fracture	No Fracture	No Fracti
Bending Te				<del> </del>	0	0	0
Evaluation	o		-0		1	<del>1</del>	4

# Table 9

No.		31	32	33	34	35	n / • <b>36</b>
Distinction		Inventive	Inventive	Inventive	Comparative	Comparative	Comparative
		Example	Example	Example	Example	Example	Example
	S	2	2	2	1	. 1 .	1
	REM	5	5	5	3	3	3
	Se	1			. 1	3	0.1
Chemical	Te	1	_	2	1	_	_
Composition	Ca	_	3	1	1	_	3 .
(wt%)	A1	_	_	_	20	_	_
	▼ ;		<b>-</b>	_		30	_
	Sn	_	_ :	- :		- · · - · <u>1</u>	20
	8	-	_		15	· · · · · ·	, <del>-</del>
	Cr	<del>-</del>	<u></u>	_		<u> </u>	15
	Ta	-	<u> </u>	-	_	_	_
	Mn	_	_	_	_	. <del>-</del>	_
	Hf	10	_		_	_	-
	W	10	-	_	_ :		
	Si	0.5	_	_	. —	_	_
	NЪ	_	20	_		_	
-	Zr	_	10	_		-	_
	Мо		_	15	· <u>-</u> -		
	0	_	<u> </u>	<del></del>	· — · · · ·	2	
	Ti	Bal.	Bal.	Bal.	Bal	Bal.	Bal.
Joining Meth	od	Friction	Friction	Friction	Friction	Friction	Friction
		Welding	Welding	Welding	Welding	Welding	Welding
Joint Streng	th	1.0	1.0	1.0	1.0	1.0	1.0
Ratio	٠.					<del></del>	
Location of							
Fracture in		No Fracture	No Fracture	No Fracture	Joint Face	Joint Face	Joint Face
ending Test	Piece				•		
Evaluation		0	0	0	Δ	. ^	- Δ

Table 10

				100	Table To			
		No.		37	38	39	40	
5	4 . S :	`		Compara- tive Exam-	Compara- tive Exam- ple	Compara- tive Exam- ple	Compara- tive Exam- ple	
	.i	Chemical	S	3	3	3	.3	
10		Composi-	REM	5	5	. 5	5	
•		tion (wt%)	Se	6	-	2	-	
• • • •		:   ·	Те	-	3	2	-	
			Ca	-	3	2	5	
15	1		Al		•	-	-	
			V	- 1	•	- <u>-</u>	•	
			Sn	* *. <del>-</del> .	•	-		
20	<b>}</b>		Co	<b>.</b>	•	-		
			Cu	•	•	-		
	·		Ta	20	•		-	
25			Mn	15			-	
20	,		Hf		15	•	-	
			W	-	15	<u> </u>		
	<b>.</b> .		Si		•	1	-	
30			Nb	-	·	23	·	
			- Zr		•	12		
		,	· Mo	-	· · · · · · · · · · · · · · · · · · ·	<u> </u>	20	
35	F	roller is.	0		<u> </u>	ļ <u>.</u>		
	1	3	Ti	Bal.	Bal.	Bal.	Bal.	
		Joining Mo	ethod	Friction Welding	Friction Welding	Friction Welding	Friction Welding	
40		Joint Strei	ngth Ratio	1.0	1.0	1.0	1.0	
		Location of in Bend	of Fracture ling Tes		Joint Face	Joint Face	Joint Face	
45		Evaluation		. Δ	Δ	Δ	. Δ	

As shown in Table 4 to table 10, in the inventive example satisfying the chemical composition defined in this invention, a joint strength ratio (ratio of joint strength to the base metal strength) showed good value respectively, and no test piece was fractured in the bending test in all of the joining methods of TIG welding, friction welding and diffusion welding, therefore good results could be obtained.

As compared with above, the bending test pieces were fractured along the fusion lines respectively in comparative alloy No. 1 which is short of S content and comparative alloy No. 2 which is short of REM content, the joint strength ratio was low and bending test piece was fractured at the joint face in comparative alloy No. 8 which is excessive in S and REM content, and the bending test piece was fractured at the fusion line in comparative alloy No. 9 which is insufficient in S, Se and REM content. In comparative alloys Nos. 17 and 18 in which S, Se and Te exceed 10 % in total, the joint strength ratios were low and the respective bending test pieces were fractured from the joint faces. Furthermore, the bending test pieces were fractured from the fusion lines respectively in comparative alloys Nos. 19 and 20 which are

insufficient in S, Se, Te, REM and Ca content, and the bending test pieces were fractured at the joint faces in comparative alloys Nos. 34 to 40 which are excessive in Al, V, Sn, Co, Cu, Ta, Mn, Hf, W, Si, Nb, Zr or Mo content.

#### Examples 41 ~ 49

Titanium alloy blocks (100 mm in diameter) having compositions shown in Table 11 and Table 12 were subjected to hot-extruding at 1000 °C using a mandrel with a diameter of 60 mm after coating vitreous lubricants on surfaces of the respective blocks, thereby manufacturing respective seamless titanium alloy pipes.

Subsequently, obtained titanium alloy pipes were subjected to the flattening test specified in JIS respectively, and productivity of the respective pipes was evaluated in a view of manufacturing efficiency. Furthermore, the penetrant inspection was carried out on outer and inner surfaces of the respective titanium alloy pipes subjected to the flattening test thereby examining the presence of crack. The results are shown together in Tables 11 and 12.

Table 11

W

No.	T	41	42	43	44	45	46
Distinction	allelot Harsi	Compara- tive Exam- ple	Compara- tive Exam- ple	Inventive Example	Inventive Example	Inventive Example	Inventive Example
Chemical	S	0.005	0.10	0.01	0.1	1	5
Composi-	REM	12	-	0.01	2	5	10
tion (wt%)	Se		-	-	•	•	
	Te	-	-	-	-	•	•
	Ca	-	-	-	-	•	
	Al	6	6	6	•	6	6
	V	4	4	4	•	4	4
	Sn	-	-	-	-	•	-
	Со	-	-	•	-	-	<u>.</u>
	Cu	-	-	•	-	-	-
	Ta	-	-	-	-	-	
	Mn	-	-	•	-	-	
	Hf	-	-	-	<u> </u>	-	
	W	-	-	•	· .	<u>.</u>	
	Si	-	-	-	-	-	<u> </u>
	Nb	-	-	-	-		<u> </u>
!	Zr	-	-	-	•	-	
1	Mo	-	-	•	•	-	<u> </u>
	0	-	-	•	-	-	-
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Manufacturin Method for F		Extruding	TIG Weld- ing	Extruding	Extruding	Extruding	Extruding
t/D		0.2	0.2	0.2	0.2	0.2	0.2
Manufacturii ciency		0	X	0	0	0	0
Flattening (Remarks)	Tes	X (Cracks)	X (Weld- ing Cracks)	0	0	0	0
Evaluation		<del>  x</del>	X	0	0	0	0

Table 12

No.		47	48	49 -
Distinction	_	Inventive Example	Inventive Example	Comparative Example
Chemical	S	10	10	15
Composition (wt%)	REM	7	10	15
(,	Se	-	-	-
	Те	-	-	•
	Ca	-	-	-
	Al	6	6	6
· ·	٧	4	4	4
7	Sn			
	Со	-	- 7-	· · · · · · · · · · · · · · · · · · ·
•	Cu	-	-	-
	Ta	-	-	-
	Mn	-	-	•
	Hf		<del>-</del>	-
	W	-	-	-
	Si	·-	-	-
	Nb	-	-	-
	Zr	•	-	•
	Мо	-	-	• • • •
	0	-	-	-
	Ti	Bal.	Bal.	Bal.
Manufacturing M for Pipe	ethod	Extruding	Extruding	Extruding
t/D		0.2	0.2	0.2
Manufacturing E ciency	ffi-	0	0	. 0
Flattening Test (Remarks)		0	0	△ (Cracks)

As is obvious from the results shown in Tables 11 and 12, the titanium alloy pipes Nos. 43 to 48 according to inventive examples were high in the manufacturing efficiency, and no crack was observed in the flattening test. As compared with the above, desirable results could not be obtained in the comparative alloy pipes No. 1 (insufficient in S and REM content) and No. 2 (lacking in REM and Ca). Furthermore, in the comparative alloy pipe No. 9, which is excessive in S and REM content, the deformability was degraded and cracks were generated in the flattening test.

O

Δ

## Examples 50 ~ 61

**Evaluation** 

Similarly to the previous examples, titanium alloy blocks (100 mm in diameter) of 12 kinds having compositions shown in Table 13 and Table 14 were subjected to hot-extruding at 1000 °C using a mardrel with 50 mm in diameter

5

10

15

20

25

30

35

40

50

after coating vitreous lubricants on surfaces of the respective blocks, thereby manufacturing seamless titanium alloy pipes of 12 kinds.

Subsequently, obtained seamless pipes were subjected to the flattening test and productivity of the respective pipes was evaluated in a view of manufacturing efficiency. Further, the presence of cracks on outer and inner surfaces of the respective pipes was examined by carrying out the penetrant inspection against the pipes after the flattening test. The results are shown together in Tables 13 and 14.

## Table 13

No.		50	51	52	53	54	55
Distinction		Comparative	Comparative	Comparative	Inventive	Inventive	Inventive
Distinction		Example	Example	Example	Example	Example	Example
		_	_	0.005	_	0.01	0.01
	REM	0.005	0.01	0.01	0.01	0.01	0.01
	Se	0.005	0.002	0.002			0.01
Chemical	Te		0.007	0.002	0.01	0.01	0.01
Composition	Ca	0.005	0.01	0.01		0.01	0.01
(wt%)	Al	6	6	6	6	6	6
(# 00)	V	4	4	4	4	4	4
	Sn	<u> </u>			_		
	Co			_	<b>–</b>	_	
	Cu		<del>  -</del>	_			
	Ta	_		_	<del>-</del>	. <u> </u>	
	Mn		š.—	-		_	
	Hf		<del></del>		_		
	W			-		<del>-</del>	
	Si	: -:	_	_			
	Nb	_	_	. –			
	Zr	ii –		_			
	Mo				<u> </u>		
	0	_	_				
	Ti	Bal	Bal.	Bal.	Bal.	Bal.	Bal.
Manufacturi	ng	Extruding	Extruding	Extruding	Extruding	Extruding	Extrudin
Method for	Pipe					<b> </b>	\
·· -t/D	_	0.25	0.25	0.25	0.25	0.25	0.25
Manufactur	ing	0	0	0	0	0	0
Efficiency			<u> </u>				<del> </del>
Flattening	Test	×	×	×	0	0	0
(Remarks)		(Cracks)	(Cracks)	(Cracks)			
Evaluation		×	×	×		. 0	0

Table 14

			· · · · · · · · · · · · · · · · · · ·				Strategy at the training
No.		56	57	58	-59	60	61
Distinction		Inventive Example	Inventive Example	Inventive Example	Inventive Example	Comparative Example	Comparative Example
Chemical	S	1	5			1	-
Composi- tion (wt%)	REM	3	4	8	-	5	<u> </u>
(**************************************	Se	0.1	-	5	10	<del>-</del>	5
	Те	0.5	2	5	-	10.	5 .
	Ca	2	3	2	10	8	15
	Al	4	4	4	4	4	4
	٧	3 :	3	3	3	3	3
	Sn	•			<u>.</u>		
	Со	•	-	•			-
	Cu	•	-	•	-	-	•
	Ta	•	-	-	-	-	
	Mn	•	-	•	-	i.	
	Hf	-		•	-		•
	W	•	•	•	-	-	
	Si	-	-	-		-	-
	Nb	•	•	-	<b>-</b>	<del>-</del>	•
	Zr	-	-	-	<b>-</b> .	<u>-</u>	-
	Мо	•	-	-	•		·
	0	•		-	• .	•	•
	Ti	Bal.	Bal.	Bal.	Bal.	Bal	_ Bal.
Manufacturi Method for I		Extruding	Extruding	Extruding	Extruding	Extruding	Extruding
t/D		0.25	0.25	0.25	0.25	0.25	0.25
Manufacturii Efficiency	ng	0	0	0	0	0	0
Flattening (Remarks)	Test	0	0	0	Ó	X (Cracks)	X (Cracks)
Evaluation		0	0	0	0	х	· X

As is evident from the results shown in Tables 13 and 14, the manufacturing efficiency was high and no crack was observed in the flattening test in the inventive alloy pipes Nos. 53 to 60. As compared with above, in the comparative alloy pipes Nos. 11 to 13 which are insufficient in S, Se, Te content and REM, Ca content, cracks were generated through the flattening test, conversely in the comparative alloy pipes No. 60 which are excessive in S, Se and Te content and in the comparative alloy pipe No. 61 which is excessive in Ca content, cracks were generated in the flattening test.

### Examples 62 ~ 78

Titanium alloy blocks (100 mm in diameter) of 17 kinds having compositions shown in Table 15 to Table 17 were subjected to hot-extruding at 1000 °C using a mandrel with 40 mm in diameter after coating vitreous lubricants on sur-

faces of the respective blocks to manufacturing seamless titanium alloy pipes.

Subsequently, obtained seamless pipes were subjected to the flattening test and productivity of the respective pipes was evaluated in a view of manufacturing efficiency. Furthermore, the presence of cracks on outer and inner surfaces of the pipes was examined by carrying out the penetrant inspection against the pipes subjected to the flattening test. The results are shown together in Tables 15 to 17.

Table 15

			Idi	016 10			
No.	<u>:</u> _	62	63	64	65	66	67
Distinction		Inventive Example	Inventive Example	Inventive Example	Inventive Example	Inventive Example	Inventive Example
Observiced	s	2	5	7	5	5	5
Chemical Composi-	REM		8	8	7	9	6
tion (wt%)	<b>├</b> ──┼		2		. 2	-	
!	Se					. 4	4
	те				2		. 3
	Ca	2	:: <b>.1</b>		6	6	
A No. 1	Al ·	4 .	. 10	.5.		4	
r	·V	- 22	20	- 25	4		
	Sn	· 3	-	- 	10	15	-
	Co			•	•		10
	Cu		-		•	<u> </u>	10
	Ta				-	•	-
	Mn			-	-	-	
	Hf			-	-	-	-
	W		<del>                                     </del>		1	-	
	Si		<del>                                     </del>			-	-
-	Nb	<u> </u>	<del>                                     </del>	<del>                                     </del>		-	-
15.			<del>                                     </del>	+	+	-	
		-	<del> </del>	<del> </del>	+	· ·	-
	Mo	ļ <u> </u>	<del></del>	<del> </del>	<del>                                     </del>	+	<del>                                     </del>
	0		Bal.	Bal.	Bal.	Bal.	Bal.
	Ti	Bal.					Extrudir
Manufactu		Extruding	Extruding	Extracting	LAUGGING		1
Method for	- he	0.3	0.3	0.3	0.3	0.3	0.3
t/D	<del></del>				10	0	0
Manufactu ciency	ıring Effi	-	O:_		· -		<del> </del>
Flattening (Remarks		1 0	0	0	0	0	0
Evaluation		0	Q	0	0	0	0
1		1	Ι'				

55

10

15

20

25

30

35

40

45

Table 16

No.		68	69	70	:71	72	73
Distinction		Inventive	Inventive				
		Example	Example	Inventive Example	Inventive Example	Comparative Example	Comparative Example
Chemical	S	5	5	5	5	5	5
Composition (wt%)	REM	7	7	7	7	7	7
•	Se	2	2	2	2	2	2
	Те	2	2	2	2	2	2
	Ca	2	2	2	2	2	2
•	Al	-	-	-	5	15	-
	V			-		20	25
	Sn	· · · .	2		2.5		15
	င	-	-	-	• .		· · -
	Cu	•	-	•	-	-	-
	Ta	15	-	-	-		· -
	Mn	10	-	-	-	-	-
	Hf	•	10	•	•	•	-
	W	•	10	•	-	-	-
	Si	-	0.5		-	-	-
	Nb	•		· 20	-	-	-
	Zr	•	•	10	-	-	
	Мо	•	•	-	15	<u>;</u> -	-
	0	-	0.1	•	-	-	7 1 -
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Manufacturing Method for Pip	e	Extruding	Extruding	Extruding	Extruding	Extruding	Extruding
₩D		0.3	0.3	0.3	0.3	0.3	0.3
Manufacturing ciency	Effi-	0	. 0	0	0	0	0
Flattening (Remarks)	Test	0	0	0	0 .	X (Cracks)	X (Cracks)
Evaluation		0	0	0	0	X	Х

5

Table 17

No.	i	74	75	· 76	77	78
Distinction with the pro-		Comparative Example	Comparative Example	Comparative Example	Comparative Example	Comparative Example
Chemical Compo-	S	5	5	5	5	5
sition (wt%)	REM	7	7	7	7	7
Cliat s	Se	2	2	2	2	2
	Те	2	2	2	2	2
	Ca	2	2	2	2	2
	Al	-	-	-	-	6
1	V <sub>1</sub> G	a :	-	-	- 1	4
j	Sn	200	***************************************			-
	Co	15	-		-	•
<b>\.</b>	Cu	-	15		-	-
	Ta	20	-	. <b>-</b>	-	-
•	Mn	<del>-</del>	15	-	-	-
	Hf		-	15		-
i <u>.</u>	W	-	10	. 15	-	<b>-</b> 1
*	Si	<u>-</u>	0.5	1	-	-
	Nb	-	-	-	22	-
	Zr	, <b>-</b>	-	-	13	-
	Мо		-	-	- :	20
· · · · · · · · · · · · · · · · · · ·	Ö	* **.	0.1	-	•	-
le2	Ti	Bal.	Bal.	Bal.	Bal.	Bal.
Manufacturing Meth	od for Pipe	Extruding	Extruding	Extruding	Extruding	Extruding
t/D		0.3	0.3	0.3	0.3	0.3
Manufacturing Efficiency		0	0 -	0	0	0
Flattening Test (Re-marks)		X (Cracks)	X (Cracks)	X (Cracks)	X (Cracks)	X (Cracks)
Evaluation		Х	Х	×	×	Х

As is obvious from the results shown in Tables 15 to 17, in the titanium alloy pipes Nos. 62 to 71 according to inventive examples of this invention, the manufacturing efficiency was high and no crack was observed in the flattening test. However, cracks was generated in the flattening test in comparative pipe No. 72 which is excessive in the total sum of Al and V content, in comparative pipe No. 73 which is excessive in the total sum of V and Sn content, in comparative pipe No. 74 which is excessive in the total sum of Co and Ta content, in comparative pipe No. 75 which is excessive in the total sum of Cu and Mn content, in comparative pipe No. 76 which is excessive in Si content and the total sum of Hi and W content, in comparative pipe No. 77 which is excessive in the total sum of Nb and Zr content and in comparative pipe No. 78 which is excessive in Mo content.

#### Examples 79 ~ 87

Titanium alloy blocks (100 mm in diameter) of 9 kinds having compositions shown in Table 18 and Table 19 were subjected to hot-extruding at a temperature between 880 and 1250 °C using mandrels having various diameters after

coating vitreous lubricants on surfaces of the respective blocks, thereby manufacturing seamless alloy pipes having various thickness.

Subsequently, obtained seamless pipes were subjected to the flattening test and productivity of the respective pipes was evaluated in a view of manufacturing efficiency. Furthermore, the penetrant inspection was carried out against outer and inner surfaces of the respective titanium alloy pipes after the flattening test in-order to examine the presence of crack. The results are shown together in Tables 18 and 19.

Table 18

No.		79	80	81	82	83
Distinction	-	Compara- tive Exam- ple	Compara- tive Exam- ple	Inventive Example	Inventive Example	Inventive Example
Chemical	S	0.01	0.01	0.01	2	5
Composition (wt%)	REM	0.01	0.01	0.01	5 ,	7
(WL 76)	Se		-	1/2	1	2
	Те	•	-	•	1'	2
	Ca	-	-	•	3	2
	Al	6	6	6	4 .	6
	V	4	4	4	22	4
	Sn	-	-			-
	Co	-	•	•	•	-
	Cu	-		•		•
	Ta	-	• .		· · · ·	-
	Mn	•	-	•		-
	Hf	-	-	-	-	-
	w	-	•	-	. <del>-</del>	
	Si	-	•	•	-	- 1
	Nb		-	•	-	•
	Zr	. • .	-	•	•	r i <u>.</u> .
	Мо	-	-	-	•	-
ļ	0	-	-	-	-	-
	Ti	Bal.	Bal.	Bal.	Bal.	Bai.
Extruding	₩D	0.4	0.5	0.4	0.4	0.3
Tempera- ture(°C)		880	900	- 900	1050	1100
Manufacturing Efficiency		Δ	Δ	0 .	0	0
Flattening Tes	Flattening Test (Remarks)		△ (Small Cracks)	· O	- 0	0
Evaluation		х	Х	0	0	0

is invensulative faither the property of the Control of the Contro

m i Paudus and Discourse Administration automorphism

5

10

15

20

25

30

35

40

45

50

wyheric:		. , , , , , , , , , , , , , , , , , , ,	JIE 19	1	
	. ,	84	85	86	. 87
Distinction		Inventive Example	Inventive Example	Compara- tive Exam- ple	Compara- tive Exam- ple
Chemical	s	7	10	10	10
Composi-	REM	10	10	10	10
tion (wt%)	Se	•		•	5
(,6)	Te	3		-	1
	Ca	·	-		3
:	Al	10	10	10	8
	V	20	20	20	10
	Sn	···		•	-
	Co	-		•	·
·	Cu	-		•	-
	Та	-	· ·	-	-
	Mn	-	-	-	•
	Hf	-	-	- <u>-</u>	·
	W.	•	T -	-	•
	Si		-	-	-
	Nb	-		-	-
	Zr	-		-	<u> </u>
	Mo		-	•	-
	0		-	-	-
	Ti	Bal.	Bal.	, Bal.	Bal.
Extruding	t/D	0.2	0.01	0.01	0.1
	Tem- pera- ture(°	1100	1150	1200	1250
Manufact ciency	uring Effi-	0	0	0	0
Flattening (Remark		0	0	△ (Small Cracks)	
Evaluatio	n ·	. 0	0	· X	X

As is apparent from the results shown in Tables 18 and 19, in the inventive pipes Nos. 81 to 85, the manufacturing efficiency was high and no crack was observed in the flattening test. As compared with above, in comparative pipe No. 79 extruded at a relatively low temperature, the productivity was not so good because of large resistance for deformation, and also in comparative pipe No. 80 of which (t/D) is relatively high, the productivity was not so good. Furthermore, in comparative pipes Nos. 86 and 87 which were extruded at a temperature not lower than 1200 °C, the crystal grains were inclined to coarsen and cracks inclusive of small cracks were generated in the flattening test.

### Examples 88 ~ 127

Titanium alloy pipes with outer diameter of 100 mm, inner diameter of 60 mm and wall thickness of 20 mm were manufactured through hot-extruding at a temperature of 1000 °C using titanium alloys having compositions shown in Table 20 to Table 26, and the titanium alloy pipes were joined through TIG welding under the condition shown in Table 1, friction welding under the condition shown in Table 2, and diffusion welding under the condition shown in Table 3, respectively. Subsequently, obtained welded joints were subjected to tensile test and bending test, and evaluated by comparing with the specific value of the respective titanium alloy base metals. The obtained results are shown together in Tables 20 to 26.

Table 20

No.		. 88	89	90	91	92	93
Distinction		Comparative	Comparative	Inventive	Inventive	Inventive	Inventive
·		Example	Example	Example	Example	Example	Example
	s	0.005	0.10	0.01	0.1	1	5
	REM	10	-	0.01	2	5	10
	Se	_	T -	_	-	<del> </del>	
Chemical	Te	_	_	_	_		<del> </del>
Composition	Ca	_	_			<del> </del> -	
(wt%) `	Al	_	_	_			6
	V		_	_			<del>                                     </del>
	Sn	_	<del>-</del>	<u> </u>	_	<del>-</del>	<del>                                     </del>
	Co	<del>-</del> .	_				<del> </del>
	Cu		_	_			<del>                                     </del>
	Ta	_		_			<del>                                     </del>
	Mrn.	_	_	_	-		1
İ	H£			_	_	_	<del>                                     </del>
	W	_		_			1 100 100
	Si		_	_	<u> </u>		<del></del>
	Nb	<del>-</del>	_	-			
	Zr	_	_	_			<del> </del>
	Mo	_	_	_		<del>                                     </del>	<del> </del>
	0	_	_	_			<del> </del>
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Joining Metho	od	TIG Welding	TIG Welding	TIG Welding	TIG Welding	TIG Welding	
Joint Streng Ratio	th	1.0	1.0	1.0	1.0	1.0	1.0
Cocation of Fracture in Ending Test I	- 1	Fused line	Fused line	No Fracture	No Fracture	No Fracture	No Fracture
valuation	<del>- 1</del>		Δ			· ·	
				0	0	0	0

Table 21

No.	- ::	nnon <b>94</b>	95	96	97	98	99
Distinction		Inventive	Comparative	Comparative	Inventive	Inventive	Inventive
राहेदा का		Example	Example	Example	Example	Example	Example
	s	10	15	0.005	0.10	0.01	0.01
•	REM	10	15	0.006	2	0.01	0.01
	Se			0.006	0.005	0.01	0.01
Chemical	Te	_	_	_	0.005		0.01
Composition	Ca	_	<del>-</del> .	-	0.005	. <del>-</del>	
(wt%)	Al .	. 6	6	_	_	_	
1 9107	V	3, 32 <b>4</b> 23	4	_	eu <del>III</del> e kir	42. <u>Table 1</u>	
2000	Sn	-	<del>-</del>	. π	<b>0.</b> 1	( <del>1   1   1   1   1   1   1   1   1   1 </del>	
01	Co	· · · · · · · · · · · · · · · · · · ·		— ·:	<del>-</del>		_
	Cu	<u> </u>		_	-		
	Ta	·	_		_		. —
	Mn	:	<u> </u>				<u> </u>
	Hf	_		_	_	.— .	. <u> </u>
\$	W			_	_	_	
	Si	`-	_	-	_	_	
6	Nb	_	_	-	_		-
	Zr	_		_	_	_	
	Мо			_	_	_	
or .	0	_	_		_	_	
	T1	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Joining Met	hod	TIG Welding	Friction	TIG Welding	TIG Welding	TIG Welding	TIG Welding
			Welding				
Joint Stren	gth	1.0	0.8	1.0	1.0	1.0	1.0
Ratio							<b></b>
Location of	.,		,	1			
Fracture in		No Fracture	Joint Face	Fused line	No Fracture	No Fracture	No Fracture
Bending Test	Piece						
Evaluation		0 -	- ×.	Δ	0		0

25 \_

. 30

# Table 22

			·	· • • • •	*		
No.		100	101	102	103	104	105
Distinction		Inventive	Inventive	Inventive	Inventive	Comparative	Comparative
		Example	Example	Example	Example	Example	Example
	S	0.1	2 .	5.	3	10	5
	REM	2	5	7	10	. 10	
	Se	0.01	0.1	2	3	5	2
Chemical	Te	0.01	_	3	4	.—	5
Composition	Ca	0.01	3	3	· –	_	10
(wt%)	Al	_	_	6	6	6 .	6
	٧ .		— <u>:</u>	. :4	4	4	4
	Sn	_ :	- :	=	<u> </u>		<del>-</del>
	Co			-	· =.	_	
	Cu	_	· –	_	_	_	_
	Ta	_	_	_	_	_	_
	Mn	<del>-</del>	_	_	_	-	_
	H£	_	· —			_	·
	W		_		_		
	Si	_	_		. –	_	
	Nb	· <del>-</del>	<del>-</del>	_	<del>.</del>	_	_
	Zr	_	_	_	·	<del>-</del>	_
	Mo	_	<del>-</del>	<del>-</del>	<b>–</b>	_	_
	0	_	_	_		. —	: -
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Joining Meth	od	TIG Welding	TIG Welding	Friction	Friction	Friction	Friction
		•		Welding	Welding	Welding	Welding
Joint Streng	th	1.0	1.0	1.0	1.0	0.9	0.8
Ratio							
Location of							
Fracture in		No Fracture	No Fracture	No Fracture	No Fracture	Joint Face	Joint Face
ending Test	Piece	,					
Evaluation		0	0	0	0	×.	×

Tabl 23

No.: 39.1	7	106	107	108	109	110	111
Distinction		Comparative	Comparative	Inventive	Inventive	Inventive	Inventive
· · · · · · · · · · · · · · · · · · ·		Example	Example	Example	Example	Example	Example
	S	0.005	0.005	0.01	0.1	1	2.
• ; • •	REM	0.005	0.005	0.01	1	2	5
	Se		0.005	0.01	_	2	. 4
Chemical	Te	_	0.005	_	1	· <b>-</b> ·	1
Composition	Ca	_	0.005		2	4	3
(wt%)	Al	6	6	4	10	6	8
(# 20)	v	3.6	.6	22	20	_	11
	Sn	-2	2			2	
	Co	-		_	···· · · · · · · · · · · · · · · · · ·	_	· · —
	Cu		-		_	· <del></del>	<u>. –                                    </u>
:	Ta		_	_	_		
÷ ,	Mn	_	_	_	_		6
*	Hf		· · · _				3
	W	-	_	_			7
	Si		-	. –	_		0.2
	Nb	<del> </del>	_		-	_	4
	Zr	_	_	<u> </u>	Ţ	4	5
• • • • • • • • • • • • • • • • • • • •	Mo	_	-	_	_	· 2	1
	0	_	-		_	<del>-</del>	<u> </u>
· · · · · · · · · · · · · · · · · · ·	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Joining Met	hod	TIG Welding	TIG Welding	TIG Welding	TIG Welding	TIG Welding	TIG Weldin
	į	94				<u> </u>	
Joint Stren		1.0	1.0	1.0	1.0	1.0	1.0
Ratio	_						
Location of		Fused line	Fused line	No Fracture	No Fracture	No Fracture	No Fractu
Bending Test	. •	ce .			,		
Evaluation			Δ	0			

# Table 24

No.		112	113	114	115	116	117
Distinction		Inventive	Inventive	Inventive	Inventive	Inventive	Inventive
		Example	Example	Example	Example	Example	Example
	S	3	7	2 .	1	2	2
	REM	4	10	7	10	3	7
	Se	_	_	5 ·	8	1	
Chemical	Te	7		3	0.01	1	5
Composition	Ca	_	_	2	_		
(wt%)	ΔĴ	_	_	7	. 4		
	▼ .			4	. 25		İ =
	Sn	<del>-</del> -	* 1995 1/ 1995 (m 1995 pr 1995	1		15	_
	Co		_	2	<del>-</del>		10
	Cu	7	_	4		_	10
	Ta	10	_	2	-	15	
	Mn.	_	_	2	. –	-	10
	Hf		_	1			<del>_</del>
	W	-		5	_	<u> </u>	_
	Si	_	_	_			
	МЬ	_	_	1			
•	Zr	ŀ	-	1		4	
1	Mo	10		_	_	2	
· [	0	0.5		_	1	. —	_
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
loining Metho	od	Friction	Diffusion	Diffusion	Friction	Friction	Priction
·		Welding	Welding	Welding	Welding	Welding	Welding
oint Strengt	h d	1.0	1.0	1.0	1.0	1.0	1.0
atio							
ocation of	ļ						
racture in		No Fracture	No Fracture	No Fracture	No Fracture	No Fracture	No Fracture
nding Test F	iece						
valuation		0	0	.0	0	0 .	0

# Table 25

<del></del>		118	119	120	121	122	123
No. Distinction		Inventive	Inventive	Inventive	Comparative	Comparative	Comparative
		Example	Example	Example	Example	Example	Example
	s	2		2	1	1 .	1
·	<del>+</del>	5	5,	5	3	3	3
•••	REM	1			1	3	0.1
	Se			2	1		_
Chemical	Te	1	3	1		_	3
Composition	Ca	<del></del>			20	_	_
(wt%)	A1					30	
7.	▼				<u> </u>		20
	Sn	77:		1			
GI	Co				15	<del></del>	15
	Cu			<del></del>		<del>                                     </del>	
ľ	Ta	<u> </u>					
· · · · .	Mn	_					<u> </u>
:·	Hf	10				<u> </u>	<u> </u>
• • • • • • • • • • • • • • • • • • • •	W	10					ļ
	Si	0.5		_			
	NЬ		20				<del>  -</del>
	Zr	, <del></del> -	·· · 10 ·	_			<del>                                     </del>
	Мо	<del>-</del>		15			
·	0					2	
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Joining Met	hod,	Friction	Friction	Friction	Friction	Friction	Friction
	eriase eriase	Welding	Welding	Welding	Welding	Welding	Welding
Joint Stren		1.0	1.0	1.0	1.0	1.0	1.0
Ratio	~		,				<u> </u>
Location of	1	No Fracture	No Fracture	No Fracture	Joint Face	Joint Face	Joint Face
Bending Test		e   O	00	0	Δ	Δ	Δ
Evaluation		.i U	ı∪	.i	1 —		

Table 26

and a light for fitting.

w sabai

1000 2001

a compare.

 $\operatorname{Spr}(P+1) = 0$ 

No. 124 125 126 Distinction Compara-Compara-Compara-Comparative Examtive Examtive Examtive Example ple pie ple Chemical Com-3 3 3 . 3. position (wt%) **REM** 5 5 5 5 Se 6 2 -Te 3 2 Ca 3 2 5 AI V Sn Co -Cu Ta 20 Mn 15 Hf \_ 15 W -15 Si \_ 1 Nb --23 -Zr 12 -Мо --20 0 Ti Bal. Bal. Bal. Bal. Joining Method Friction Friction Friction Friction Welding Welding Welding Welding Joint Strength Ratio 1.0 1.0 1.0 1.0 Location of Fracture in Bend-Joint Face Joint Face Joint Face Joint Face ing Test Piece **Evaluation** Δ Δ Δ Δ

As shown in Tables 20 to 26, in the inventive example satisfying the chemical composition defined in this invention, a joint strength ratio showed high value respectively, and no test piece was fractured in the bending test in all of the joining methods of TIG welding, friction welding and diffusion welding, therefore good results could be obtained.

As compared with above, in comparative alloy pipe No. 88 which is short of S content and comparative alloy pipe No. 89 which is short of REM content, the bending test pieces were fractured from the fusion lines respectively, and the joint strength ratio was low and the bending test piece was fractured at the joint face in comparative alloy pipe No. 95 which is excessive in S and REM content. The bending test piece of comparative alloy pipe No. 96 which is insufficient in S, Se and REM content was fractured at the fusion line, the joint strength ratios were low and the respective bending test pieces were fractured from the joint faces in comparative alloy pipes Nos. 104 and 105 of which total sum of S, Se and Te exceeds 10 %, and the bending test pieces were fractured from the fusion lines respectively in comparative alloy pipes Nos. 106 and 107 which are insufficient in S, Se, Te, REM and Ca content. Furthermore, in comparative alloy pipes Nos. 121 to 127 which are excessive in Al, V, Sn, Co, Cu, Ta, Mn, Hf, W, Si, Nb, Zr or Mo content, the bending test

5

10

15

20

25

30

35

40

pieces were fractured from joint faces.

## Examples 128 ~ 136

5

Titanium alloy pipes having various wall thicknesses were manufactured through hot-extruding at a temperature of 1000 °C using titanium alloys having composition shown in Table 27 and Table 28 with mandrels having various diameters, and the titanium alloy pipes were joined with each other through TIG welding, friction welding and diffusion welding under the respective conditions shown in Tables 1 to 3. Subsequently, obtained welded joints were subjected to tensile tent and bending test, and evaluated by comparing with the specific value of the respective titanium alloy base metals. The results are shown together in Tables 27 and 28.

Table 27

						· · · · · · · · · · · · · · · · · · ·	
No.		128	129	130	131	132	·· 133
Distinction		Comparative	Comparative	Inventive	Inventive	Inventive	Inventive
		Example	Example	Example	Example	Example	Example
	S	0.1	0.2	0.01	0.1	2	5
	REM	_	1.0	0.01	0.3	5	8
	Se	0.1	0.1	<del>-</del>	0.1	. –	2
Chemical	Te	_	0.1	-	0.1	1	_
Composition	Ca	_	0.4	_	0.1	2	1
(wt%)	Al	6	6	_	6	4 .	10
	V	, 4 ~	4 .	_	4	. 22	20
	Sn	_		** ************************************		3	. –
	Co	_		<u> </u>		·	_
	Cu		_		-:	_	-
	Ta	_	. —	_	_		
	Mn	_			_	· _	
	Hf	_	_	_		_	. · <b>–</b>
	W	_	_	-	_		_
	Si	_	_		_	_	
	Мр	_	_	<b>—</b> .	<b>—</b> .	÷	_
	Zr	_	_	_	<u> </u>	_	
	Mo	_	_	_	<del>-</del>	_	_
	0	_	_			· _	_
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Manufacturin	ß	Extruding	Extruding	TIG Welding	Extruding	Extruding	Extruding
Method for F	Pipe						 
t/D		0.2	0.005	0.01	0.1	0.2 11.11	0.3
Joining Meth	od	TIG Welding	TIG Welding	TIG Welding	Friction	Friction	Diffusion
			-		Welding	Welding	Welding
Joint Strength		1.0	1.0	1.0	1.0	1.0	1.0
Ratio				·			
Location of							
Fracture in Fused lin		Fused line	Fused line	No Fracture	No Fracture	No Fracture	No Fractu
Sending Test	Piece						
Evaluation	<u> </u>	- Δ	Δ	0	. 0	0	0
							L

Table 28

		. No		134	135	136
5		Distinction	· · ·	Inventive Example	Comparative Example	Comparative Example
		Chemical	S	5	5	15
	e e e e e e e e e e e e e e e e e e e	Composition	REM	7	7	15
10		(wt%)	Se	2	2	-
		ļ	Te	1	1	-
			Ca	3	3	•
15	••		Al	4	4	6
	.55	1 50	V	. 22	22 2	4 +
		2	Sn	4	4	<u>.</u>
	months plant - 1 x 1 x 2 x		Co.	•	-	-
20	, .		Cu	-		-
	•		Та	•		•
			· Mn		-	-
25	<i>i</i> .		Hf	-	-	
			W		-	-
	٠.		Si			•
	;		Nb	-	-	•
30			Zr .		-	-
	* 1		. Mo			-
	3311	1 . (35	0	•		-
35	gardura)	<b>11.</b> 1 3/12 4/11 1	Ti	Bal.	Bal.	Bal.
		Manufacturin	g Method	Extruding	Extruding.	Extruding
		for Pipe			· · · · · · · · · · · · · · · · · · ·	
40	4	t/D		0.4	0.45	0.2
40		Joining Meth	od	Diffusion Welding	Diffusion Welding	Diffusion Welding
		Joint Strengt	h Ratio	1.0	1.0	1.0
45	· · · · · · · · · · · · · · · · · · ·	Location of F Bending Test	racture in	No Fracture	Joint Face	Joint Face
		Evaluation		0	· X	X
	•			<u> </u>		

### Examples 137 ~ 145

Titanium alloy blocks (100 mm in diameter) having compositions shown in Table 29 and Table 30 were coated with vitreous lubricants on the surfaces thereof and subjected to hot-extruding at a temperature between 880 and 1250 °C using mandrels having various diameters to manufacture the titanium alloy pipes having various wall thicknesses, and the titanium alloy pipes were jointed with each other through TIG welding, friction welding and diffusion welding under the respective conditions as shown in Tables 1 to 3. The obtained joints were subjected to tensile test and bending test, and evaluated by comparing with the specific valued of the respective titanium alloy base metals. The obtained results

are shown together in Tables 29 and 30.

Table 29

						.0:17		
No.		137	138	139	140	141	142	
Distinction		Comparative	Comparative	Inventive	Inventive	Inventive	Inventive	
	,	Example	Example	Example	Example	Example	Example	
	S	0.01	<u> </u>	0.01	2	5	7	
	REM	0.01	_	0.01	5	7	10	
	Se		0.01		1	2	_	
Chemical	Te	_	_		1	2	3	
Composition	Ca	_	0.01	<del>-</del>	. 3	2	<del>  _</del>	
(wt%)	Al	6	6	6	4	6	10	
	V	4	. 4	4	22	4	20	
	Sn	_	-	_	- :		<del>                                     </del>	
	Co	_	_	<u> </u>		<del>                                     </del>	<del> </del>	
	Cu		_	_			<u> </u>	
	Ta	_			: <u>-</u> -	<del> </del>	<del> </del>	
	Mn		_		_	<del>†</del>	<u> </u>	
	Hf	-				<del>                                     </del>	<del> </del>	
	W	_	_			<del>                                     </del>		
	Si	_	_	_				
	Мb	_	_			<del>  -</del>	<del> </del>	
	Zr	_	. —	_			<del>                                     </del>	
·	Mo	_	_ ·	_	_: -		<del> </del>	
	0	<u> </u>	_	_		_		
	Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	
Extruding		880	900	900	1050	1100	1100	
Temperature	(°C)						,	
t/D		0.4	0.5	0.4	0.4	0.3	0.2	
Joining Metho	od	TIG Welding	TIG Welding	TIG Welding	Diffusion	Diffusion	Diffusion	
		-			Welding	Welding		
Joint Strength 0.95		. 0.98	1.0	1.0	1.0	Welding		
Ratio					1.0	1.0	1.0	
Location of					•		-	
		Fused line	No Fracture	No Fracture	No Process			
ending Test P	iece			FIGURE	m riacture	No Fracture	No Fracture	
Svaluation		×					·	
Svaluation		×	×	0	0	0	0	

Table 30

			<u> </u>		
No.		143	144	145	
Distinction		Inventive	Compara- tive Example	Compara- tive Example	
Chemical	S		10	10	
Composi- tion (wt%)	REM	10	10	10	
uon (wing)	Se	-	-	5	
	Те	-	-	1	
	Ca	-	-	3	
,	Al	10	10	8	
	V	20	20	10	
	Sn	# # # # # # # # # # # # # # # # # # #	The state of the s	t t strenge men e were to	
	Co		-		
	Cu		<u>-</u>	-	
	Ta	-	-	-	
	Mn	-	•	-	
	Hf	-	-	-	
•	W		•	-	
	Si	-	<u>.</u>	-	
	Nb	•	•		
	.: Zr	•	-	•	
	. Mo	•	-	-	
	; O	-	., . <del>-</del>	-	
!	Ti	Bal.	Bal.	Bal.	
Extruding 1 ture (°C)	Tempera-	1150	1200	1250	
<b>t/</b> D ,		0.01	0.01	0.1	
Joining Metho	od	TIG Welding	Friction Welding	Friction Welding	
Joint Strength	Ratio	1.0	1.0	1.0	
Location of Fr Bending Test		No Fracture	Joint Face	Joint Face	
Dending rest					

Examples 146 ~ 155

Titanium alloy pipes with outer diameter of 100 mm, inner diameter of 80 mm and wall thickness of 10 mm were manufactured through hot-extruding at a temperature of 1000 °C using titanium alloy blocks having compositions shown in Table 31 and Table 32, and the titanium alloy pipes were joined in a vacuum after inserting either alloy A (Ti - 40Zr - 15Cu - 10Ni, melting point : 830 °C) or alloy B (Ti - 35Zr - 15Cu - 15Ni, melting point : 820 °C) in a form of evaporation layer, sheet or powder between joint faces of the respective alloy pipes. Subsequently, the obtained joints were subjected to tensile test and evaluated by comparing with the specific value of the respective alloy base metals. The results

are shown together in Tables 31 and 32.

In this case, the evaporation layer (joint layer) or the sheet (joint metal) were arranged as shown in FIG.1. In FIG.1, numerals 1 and 3 indicate the titanium alloy pipes, numeral 10 indicates the joint layer or the joint metal and numeral 11 indicates the joint member.

Additionally, high-frequency induction heating at 20 kHz was used for heating in a vacuum, and the pipes were applied with welding pressure of 10 MPa after being held at joining temperature for 300 sec.

## Table 31

No.			146	147	148	149	150	151 :
Distinction		Comparative	Comparative	Inventive	Inventive	Inventive	Inventive	
		<b>.</b>	Example	Example	Example	Example	Example	Example
		S	-	0.005	0.1	2	5	_
	Ī	REM	_	0.005	0.1	5	7	4
	Ī	Se	— "	·	<del>-</del>		2	5
Chemic	cal	Te	—	_	— ·	1	2	5
Compos	sition	Ca		_	_	3	2	6
(wt%)		Al	6	6	6	4	6	6
	İ	V	4	. 4	4	22	4	4 .
		Sn		_	_	_	· <u>·</u> ·	_ ·
		œ	_		_	_	_	_
•		Cu	-	<del>-</del>	_		_	_
		Ta	_	_	_	<del>-</del>	_	<del></del> :
		Mn		<b>–</b> .	_	-	· — .	·
		Hf	_ ·	_			· —	
		Я	_	_	_		<del></del> -	· <del>_</del>
		Si	` -	_	-			-
		Nb	-		-	<u>-</u>	,	_
		Zr		<del>-</del>	_	_		- 1
		Mo	_	_	_		· <del></del> , ra	
		0	_	<del></del>	_			** \$ <u>**</u> *
		Ti	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Joint	Allo	У	A	A	A	В	В	A
Layer	Thickn	ess	10	20	20	30	40	50
or	(μ <b>=</b>	)				_		·
<b>f</b> etal	Arrange	ment	FIG. 1A	FIG.1B	FIG.1C	FIG.1D	FIG.1E	FIG.1E
Joini	ng		900	800	850	950	900	930
Тевре	rature	(3)				-		
Joint Strength		0.8	0.6	1.0	1.0	1.0	1.0	
Ratio								
Location of		Base Metal	Joint Face	Base Metal	Base Metal	Base Metal	Base Metal	
Fracture								
Evalu	ation		×	×	0	0	0	0
Renar	ks		* fracture	from crack e	existing on th	e surface of	pipe	

in the control of subsections and the control of th

					·				
			No.		152	153	154	155	
	231	•	Distinction		Inventive Example	Inventive Example	Comparative Example	Comparative Example	
			Chemical	S	-	-	5	-	
			Composition (wt%)	REM	4	4	10	4	
			(441,0)	Se	5	5	5	5	
••	<u>.</u>		• • • • • •	Те	5	5	5	5	
	• :			Ca	6	6	5	10	
				Al .	6	6	6	6	
	1		·	<b>y</b>	4	. 4 :	2 4 1	4 <sub>†</sub>	
	ŀ		-	Sn				-	
	}		<b>d</b>	Co- · `		·-	-	· -	
			:	Cu	. ""	. <del>-</del> .	-	-	
		·		Ţa	. <b>-</b>	-	•	-	
	•			Mn	, <u>.</u>	•	•	•	
				Hf	-	-	•	-	
	•			W	•	-		~	
				Si	-	-	•	-	
			*** * ** *	, Ņb,	<del></del>	-	-	-	
	en:			Zr	·	-	-	-	
	۶: :			Mo	-	-	<u>.</u>	-	
				0	<u>-</u>	•	•		
	ĺ			Ti	Bal.	Bal.	Bal.	Bal.	
		.	Joint Layer or Metal	Alloy	Α	. В	В	Α	
	•	٠	Of Wetai	Thick- ness (µm)	1	100	20	0.5	
	•			Arrange- ment	FIG.1B	FIG.1A	FIG.1A	FIG.1A	
		٠. ا	Joining Tempe	erature (°C)	840	940	900	900	
		j	Joint Strength	Ratio	1.0	1.0	0.8	0.8	
			Location of Fra	acture	Base Metal	Base Metal	Joint Face	Joint Face	
			Evaluation		. 0	Ο.	X	Х	
		•			1				

#### Examples 156 ≈ 161

Titanium alloy pipes with outer diameter of 100 mm, inner diameter of 80 mm and wall thickness of 10 mm were manufactured through hot-extruding at a temperature of 1000 °C using titanium alloy blocks having compositions shown in Table 33. The titanium alloy pipes were formed with joint layers with compositions shown in the table on the joint faces of the respective pipes, and joined with each other at different temperatures. Subsequently, the obtained joints were subjected to tensile test and evaluated by comparing with the specific value of the respective alloy base metals. The results are shown together in Table 33.

In this case, the pipes were applied with welding pressure of 10 MPa after being held at joining temperature for 300 sec in a vacuum.

### Table 33

•	•			•			÷ · · · · ·	
No.		156	157	158	159	160	161	1
Distinction  Base Metal		Comparative Example	Inventive Example	Inventive Example	Inventive Example	Inventive Example	Comparative Example No. 154	
		No. 148	No. 148	No. 150	No. 151	No. 153		
Composition	Ti	30	20	35	35	50	50	
of	Zr	10	20	35	35	40	45	
Joint Layer	Cu	50	59	15	15	9	5	
(wt%)	Ni	10	1	15	15	1	0	_
Thickness (µ n)		5	5 <sup>;</sup>	10	10	20	20	
Melting Point(℃)		730	780	<b>820</b> .	820	1030	1050	
Arrangement		FIG.1B	FIG. 1B	FIG. 1C	FIG.1C	FIG.1D	FIG.1D 2 1	zi.
Joining Temperature (°C)		900	900	900	900	1100	1100	
Joint Strength Ratio		0.6	1.0	1.0	1.0	1.0	0.8	
Location of Fracture		Joint Face	Base Metal	Base Metal	Base Metal	Base Metal	Joint Face	
Evaluation		×	0	0	0	0.	×	Ì

#### Examples 162 ~ 167

5

10

15

20

25

30

35

45

50

55

Titanium alloy pipes with outer diameter of 100 mm, inner diameter of 80 mm and wall thickness of 10 mm were the standard manufactured through hot-extruding at a temperature of 1000 °C using titanium alloy blocks having compositions shown in Table 34. The titanium alloy pipes were formed with joint layers shown, in the table on the joint faces of the respective pipes and joined with each other by high-frequency induction heating of different frequencies. The obtained joint were subjected to tensile tent and evaluated by comparing with the specific value of the respective titanium alloy base metals. The results are shown together in Table 34.

in a law & Collegeoted to text 1 ....

In this case, the pipes were applied with welding pressure of 10 MPa after being held at joining temperature for 300 sec in a vacuum.

Table 34

No.		162	163	164	165	166	167	
Disti	nction	Comparative	Comparative	Inventive	Inventive	Inventive	Inventive	
		Example	Example	Example	Example	Example	Example	
Base Metal		No. 147	No. 148	No. 149	No. 150	No. 151	No. 153	
Joint	Composition	- No. 157	No. 157	No. 157	No. 158	No. 159	No. 160	
Layer	Thickness (µm)	5	5	10	15	20	30	
4.	Arrangement	FIG.1A	FIG. 1A	FIG.1B	FIG.1C	FIG. 1D	FIG.1E	
Frequency (kHz)		400	400	200	100	25	3	
Joining		900	900	900	900	900	1100	
Tempe	erature (°C)	19,04	2 057				<u> </u>	
Joint Strength		0.8	0.9	1.0	1.0	1.0	1.0	
Ratio	,					!		
Location of		Joint Face	Joint Face	Base Metal	Base Metal	Base Metal	Base Metal	
Fracture				٠.		]		
Evalu	ation	×	· ×	0	0	0	0	

#### Examples 168 ~ 173

Strain Control of Strain But to the Control

Parties of Harrison Company of

5

10

15

20

25

40

45

50

55

Titanium alloy pipes with outer diameter of 100 mm, inner diameter of 80 mm and wall thickness of 10 mm were manufactured through hot-extruding at a temperature of 1000 °C using titanium alloy blocks having compositions shown in Table 35. The titanium alloy pipes were joined with each other changing the joining atmosphere, and the obtained joints were subjected to tensile test and evaluated by comparing with specific value of the respective titanium alloy base metals. The results are shown together in Table 35.

In this case, the pipes were heated for 300 sec. through high-frequency induction heating at frequency of 20 kHz and applied with welding pressure of 10 MPa.

### Table 35

							•	<u>.</u>
No.			168	169	170	171	172	··· 173 - ·
Distinction  Base Metal		Comparative	Inventive	Inventive	Inventive	Inventive	Comparative	
			Example	Example	Example	Example	Example	Example
		No. 148	No. 148	No. 149	No. 150	No. 151	No. 153	
oint		sition	No. 157	No. 157	No. 158	No. 159	No. 160	No. 157
ayer	Thickness (µm)		10	10	20	20	20	20
acy car								
			FIG.1B	FIG. 1B	FIG. 1C	FIG.1D	FIG.1E	FIG.1B
Joining		•	900	900	900	900	1100	900
Temperature (°C)		e (°C)						1.2.2.1.1.
Atmosphere gas			Ar -	Ar	He	Vacuum	Ar Ar	Ar
		02	0.1	0.01	0.005		0.005	: 0.01B
		(vo! %)		ļ				
		N <sub>2</sub>	0.1	0.01	0.01	_	0.005	0.10
		(vo! %)	·				4)1-	A - 1 1 1 1 1 1 1 1
Joint Strength		0.9	1.0	1.0	1.0	1.0	0.9	
Rati	o					<u> </u>		<u> </u>
Location of		Joint Face	Base Metal	Base Metal	Base Metal	Base Metal	Joint Face	
Fracture					<u>'</u>			
Eval	uation	1	×	0	0	0,	0	×

#### Examples 174 ~ 178

5

10

15

20

25

30

35

45

50

55

Titanium alloy pipes with outer diameter of 100 mm, inner diameter of 80 mm and wall thickness of 10 mm were manufactured through hot-extruding at a temperature of 1000 °C using titanium alloy blocks having compositions shown in Table 36. The titanium alloy pipes were jointed with each other under the similar conditions shown in Table 35 after forming inclined planes at ends of the respective pipes. Subsequently, the welded joints were subjected to tensile test and evaluated by comparing with the specific value of the respective titanium alloy base metals. The results are shown together in Table 36.

art, en av. di. 145. 27 til

Additionally, in FIG. 2, numerals 1 and 3 indicate the titanium alloy pipes, numeral 10 indicates the joint layer or joint metal, and numeral 11 indicates the joint member.

Table 36

No	174	175	176	177	178
Distinction	Inventive Example	Inventive Example	Inventive Example	Inventive Example	Inventive Example
Combination of Joining Conditions	No. 169	No. 169	No. 170	No. 171	No. 172
Arrangement	FIG.1A	FIG.2A	FIG.2B	FIG.2C	FIG.2D
Joint Strength Ratio	1.0	1.0	1.0	1.0	1.0
Location of Fracture	Ease Metal	Base Metal	Base Metal	Base Metal	Base Meta
Bending Test	16 O	L POAT O	······································	0	··· • • • • • • • • • • • • • • • • • •
Evaluation 3	00 n O t	0	<b>©</b>	0	0

An example of the joining apparatus for execution of this invention is shown in FIG.3.

In the joining apparatus shown in FIG.3, numerals 1 and 3 are the titanium alloy pipes, numerals 2 and 4 are fixed and movable chucks as a pressing means, numeral 5 is an induction coil as a heating means, numeral 6 is a radiation thermometer as a temperature measuring means, numeral 7 is a pressure gauge as a pressure measuring means and numeral 8 is a controller as a control means.

As mentioned above, in the titanium alloy or the titanium alloy pipe according to this invention, which contains one or more of 0.01 to 10 wt% of S, 0.01 to 10 wt% of Se and 0.01 to 10 wt% of Te within a range of not exceeding 10 wt% in the total sum of S, Se and Te, and one or both of 0.01 to 10 wt% of REM and 0.01 to 10 wt% of Ca within a range of not exceeding 10 wt% in the total sum of REM and Ca, an excellent effect can be obtained since the coarsening of the crystal grain at a temperature higher than  $\alpha$ - $\beta$  transition temperature is inhibited and it is possible to prevent the mechanical properties from the deterioration caused by welding or hot-extrusion. The titanium alloy or the titanium alloy pipe according to this invention can be improved in the strength by further containing one or more of Al, V, Sn, Co, Cu, Ta, Mn, Hf, W, Si, Nb, Zr, Mo and O in the predetermined range.

In the method for producing the titanium alloy pipe according to this invention, the titanium alloy material having the aforementioned chemical composition is extruded into a seamless tubular shape. Therefore, wastage of the extruding die can be reduced and it is possible to provide titanium alloy pipes having good surface quality and excellent in the flattening test property and possible to especially provide thick-walled titanium alloy pipes applicable to the large-sized structures.

In an embodiment of the method for producing the titanium alloy pipe according to this invention, it is possible to produce the thick-walled titanium alloy pipes without applying excessive pressure by extruding the titanium alloy material into the tubular shape so that the ratio (t/D) of thickness (t) to outer diameter (D) of the pipe may be in a range of 0.01 to 0.4. Further in the other embodiment of the method for producing the titanium alloy pipe according to this invention, it is possible to reduce deformation resistance at the time of hot-extruding and possible to produce the seamless titanium alloy pipes without coarsening of crystal grain by extruding the titanium alloy material at a temperature range of 900 °C to 1150 °C.

In the joined tubular body according to this invention and formed by joining the titanium alloy pipes having the aforementioned chemical compositions with each other, it is possible to improve the quality of the welded joint even in the welding at the job site, and possible to provide large-scaled and thick-walled joined tubular bodies applicable to the large-sized structures.

In the method for producing the joined tubular body according to this invention, and comprising the steps of forming the joint layer of which melting point  $(M_I)$  is lower than melting point  $(M_M)$  of titanium alloy pipes to be joined on one or both joint faces of the pipes, and/or inserting the joint metal or the joint member between the joint faces, the joint metal having melting point  $(M_I)$  lower than melting point  $(M_M)$  of the pipes and the joint member being previously formed with joint layers of which melting point  $(M_I)$  is lower than melting point  $(M_M)$  of the pipes on both ends thereof, and joining the pipes by heating the pipes at a temperature (T) higher than  $(M_I)$  and lower than  $(M_M)$  and holding the pipes at the temperature (T) for a predetermined period at the same time of applying pressure on the joint faces of the pipes, it is possible to join the pipes securely with each other even in the welding at the job site, and possible to produce the joined

5

10

15

20

A N

tubular body applicable to the large-sized structures.

#### Claims

10

15

20

25

35

40

45

50

55

- An titanium alloy consisting essentially by weight percentage of not more than 10 % in total sum of at least one element selected from 0.01 to 10 % of S, 0.01 to 10 % of Se and 0.01 to 10 % of Te, not more than 10 % in total sum of one or both of 0.01 to 10 % of REM and 0.01 to 10 % of Ca, and the remainder being substantially Ti.
- 2. A titanium alloy consisting essentially by weight percentage of not more than 10 % in total sum of at least one element selected from 0.01 to 10 % of S, 0.01 to 10 % of Se and 0.01 to 10 % of Te, not more than 10 % in total sum of one or both of 0.01 to 10 % of REM and 0.01 to 10 % of Ca, not more than 30 % in total sum of at least one element selected from not more than 10 % of Al, not more than 25 % of V, not more than 15 % of Sn, not more than 10 % of Co, not more than 10 % of Cu, not more than 15 % of Ta, not more than 10 % of Mn, not more than 10 % of Hf, not more than 10 % of W, not more than 0.5 % of Si, not more than 20 % of Nb, not more than 10 % of Zr, not more than 15 % of Mo and not more than 0.1 % of O, and the remainder being substantially Ti.
  - 3. A titanium alloy pipe characterized by being formed of the alloy according to claim 1.
  - 4. A titanium alloy pipe characterized by being formed of the alloy according to claim 2. A titanium alloy pipe characterized by being formed of the alloy according to claim 2.
  - 5. A titanium alloy pipe as set forth in claim 3 or 4, wherein said pipe is seamless.
  - 6. A titanium alloy pipe as set forth in claim 3, 4 or 5, wherein a ratio (t/D) of thickness (t) to outer diameter (D) of the pipe is not less than 0.01 and not more than 0.40.
  - A method for producing the titanium alloy pipe according to claim 5, characterized by extruding a titanium alloy material having the composition according to claim 1 or 2 into a seamless tubular shape.
- 8. A method for producing the titanium alloy pipe as set forth in claim 7, wherein said titanium alloy material is extruded into the tubular shape of which ratio (t/D) of thickness (t) to outer diameter (D) is not less than 0.01 and not more than 0.40.
  - 9. A method for producing the titanium alloy pipe as set forth in claim 7 or 8, wherein said titanium alloy material is extruded at a temperature not lower than 900 °C and not higher than 1150 °C.
  - 10. A method for producing the titanium alloy pipe as set forth in claim 9, wherein said titanium alloy material is extruded using a vitreous lubricant.
  - 11. A joined tubular body characterized in that titanium alloy pipes according to claim 3 are joined with each other.
  - 12. A joined tubular body characterized in that the titanium alloy pipes according to claim 4 are joined with each other.
  - 13. A joined tubular body characterized in that the titanium alloy pipes according to claim 3 and claim 4 are joined with each other.
  - 14. A joined tubular body as set forth in claim 11, 12 or 13, wherein said pipes are seamless.
  - 15. A joined tubular body as set forth in any one of claims 11 to 14, wherein a ratio (t/D) of thickness (t) to outer diameter (D) of each of pipes is not less than 0.01 and not more than 0.40.
  - 16. A method for producing the joined tubular body according to any one of claims 11 to 15 which comprises the steps of :

forming a joint layer of which melting point  $(M_i)$  is lower than melting point  $(M_M)$  of the titanium alloy pipes to be joined with each other on one or both of joint faces of said titanium alloy pipes; and joining the titanium alloy pipes with each other by heating said pipes at a temperature (T) higher than  $(M_i)$  and lower than  $(M_M)$  and holding said pipes at the temperature (T) for a predetermined period at the same time of applying pressure on said joint faces of the titanium alloy pipes to be jointed with each other.

- 17. A method for producing the joined tubular body according to any one of claims 11 to 15, which comprises the steps of
  - inserting a joint metal of which melting point  $(M_l)$  is lower than melting point  $(M_M)$  of the titanium alloy pipes to be joined with each other between joint faces of said titanium alloy pipes; and
  - joining the titanium alloy pipes with each other by heating said pipes at a temperature (T) higher than  $(M_I)$  and lower than  $(M_M)$  and holding said pipes at the temperature (T) for a predetermined period at the same time of applying pressure on said joint faces of the titanium alloy pipes to be joined with each other.
- 18. A method for producing the joined tubular body according to any one of claims 11 to 15, which comprises the steps of:
  - forming a joint layer of which melting point  $(M_i)$  is lower than melting point  $(M_M)$  of the titanium alloy pipes to be joined with each other on one or both of joint faces of said titanium alloy pipes; inserting a joint metal of which melting point  $(M_i)$  is lower than melting point  $(M_M)$  of the titanium alloy pipes to be joined with each other between said joint faces of the titanium alloy pipes; and joint the titanium alloy pipes with each other by heating said pipes at a temperature (T) higher than  $(M_i)$  and
  - joining the titanium alloy pipes with each other by heating said pipes at a temperature (T) higher than  $(M_I)$  and lower than  $(M_M)$  and holding said pipes at the temperature (T) for a predetermined period at the same time of applying pressure on said joint faces of the titanium alloy pipes to be joined with each other.
  - 19. A method for producing the joined tubular body according to any one of claims 11 to 15, which comprises the steps of :
    - inserting a joint member between joint faces of the titanium alloy pipes to be joined with each other, said joint member being previously formed with joint layers of which melting point  $(M_I)$  is lower than melting point  $(M_M)$  of said titanium alloy pipes on both end faces thereof; and joining the titanium alloy pipes with each other by heating said pipes at a temperature (T) higher than  $(M_I)$  and lower than  $(M_M)$  and holding said pipes at the temperature (T) for a predetermined period at the same time of applying pressure on said joint faces of the titanium alloy pipes to be joined with each other.
  - 20. A method for producing the joined tubular body as set forth in claim 17 or 18, wherein said joint metal has a thickness of not less than 1 μm and more than 100 μm.
- 21. A method for producing the joined tubular body as set forth in claim 16, 18 or 19 wherein said joint layer has a thickness of not less than 1 μm and not more than 100 μm.

16-11

- 22. A method for producing the joined tubular body as set forth in claim 17, 18 or 20, wherein said joint metal consists essentially of Ti, Zr, Cu and Ni with the proviso that Ti and Zr are not less than 20 wt% respectively, the total sum of Ti and Zr is not less than 40 wt% and not more than 90 wt%, and the total sum of Cu and Ni is not less than 10 wt% and not more than 60 wt%.
- 23. A method for producing the joined tubular body as set forth in claim 16, 18, 19 or 21, wherein said joint layer consists essentially of Ti, Zr, Cu and Ni with the proviso that Ti and Zr are not less than 20 wt% respectively, the total sum of Ti and Zr is not less than 40 wt% and not more than 90 wt%, and the total sum of Cu and Ni is not less than 10 wt% and not more than 60 wt%.
- 24. A method for producing the joined tubular body as set forth in any one of claims 16 to 23, wherein said pipes are heated at the temperature (T) through high-frequency induction heating in a frequency not higher than 200 kHz.
- 25. A method for producing the joined tubular body as set forth in any one of claims 16 to 24, wherein said pipes are joined by heating and holding the pipes at the temperature (T) in a vacuum or an inert gas of which oxygen content and nitrogen content are not higher than 0.01 % in volume, respectively.
- 26. A method for producing the joined tubular body as set forth in any one of claims 16 to 25, wherein said pipes are joined in a state where the joint faces of the pipes are inclined.
  - 27. A method for producing the joined tubular body as set forth in any one of claims 16 to 26, wherein said pipes are joined by using a joining apparatus provided with a heating means for heating the joint faces of said titanium alloy pipes, a temperature measuring means for measuring a temperature at the joint faces of said pipes, a pressing

5

15

20

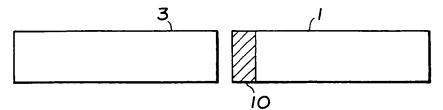
25

30

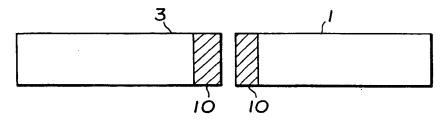
40

means for applying pressure on the joint faces of said pipes, a pressure measuring means for measuring the pressure applied on the joint faces of said pipes and a control means for controlling said respective means.

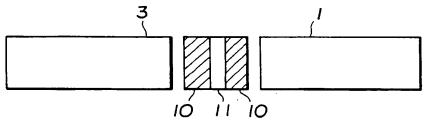
### FIG.1A



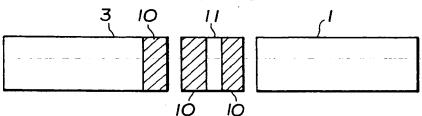
# FIG.1B



# FIG.1C



# FIG.1D



### FIG.1E

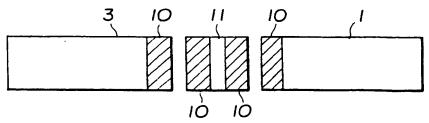


FIG.2A

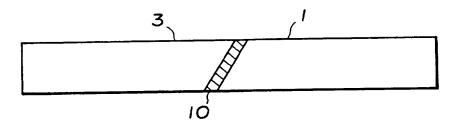


FIG.2B

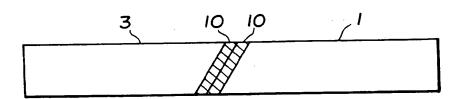


FIG.2C

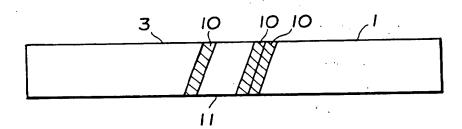
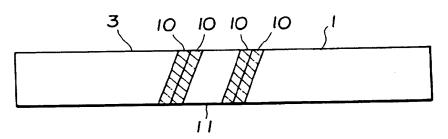
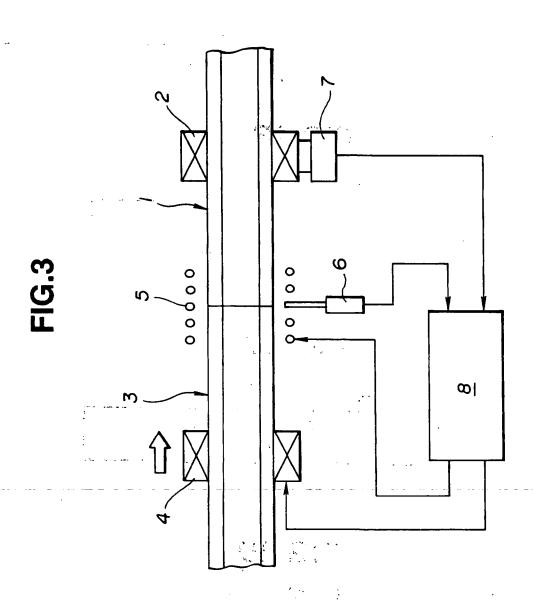


FIG.2D







### EUROPEAN SEARCH REPORT

Application Number EP 96 10 8929

3	DOCUMENTS CONSID		ANT	•	i ''
Category	Citation of document with ind of relevant pass	ication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL6)	F. :
Х	EP-A-0 199 198 (DAID October 1986 * claims 1,2; tables		1,2	C22C14/00 B23K35/32	
X	EP-A-0 202 791 (DAID November 1986  * claim 3 *		1,2		nimena (ji
A	EP-A-0 456 481 (DAII November 1991 * claim 1 *	00 STEEL CO LTD) 13	22,23		We trust
					. N.T
				TECHNICAL FIELDS SEARCHED (Int.Cl.6)	
			į	C22C B23K	
				range and the second	*
		÷			
		·			
	The present search report has	neen drawn up for all claims			
-	Place of search	Date of completion of the se	erch'	Pacaminer	•
Î	THE HAGUE	21 August 19	96	Gregg, N	
Y:	CATEGORY OF CITED DOCUMI particularly relevant if taken alone particularly relevant if combined with a document of the same category technological background non-written disclosure	CNTS T: theory of E: earlier; sfrer the counter D: document L: document	r principle underlying atent document, but a filing date not cited in the applicationed for other reasons.	published on, or	